

11 Stability of Dispersions

The flocculation of dispersions is a consequence of attractive forces holding particles together when they collide. If the particles repel each other sufficiently strongly, they bounce apart on collision and the dispersion is free from coagulation and stable. The quantitative theory for the stability was independently developed by Derjaguin and Landau in the U.S.S.R. and Verwey and Overbeek in the Netherlands and is called the DLVO theory. This theory provides a fundamental framework, with which to discuss the stability of dispersions. However, we must note that this theory works best for ideal model materials since ions treated in the theory are considered as point charges which do not readily form chemical complexes (Matijević, 1973). The hydration forces observed, for instance, between mica surfaces are caused by adsorption of hydrated species (ions) rather than by the inherent nature of the surface (Pashley and Quirk, 1984). In particular, an application of the DLVO theory to the stability of emulsions is questionable, since there are usually emulsifying agents at the interfaces.

11.1 DLVO Theory

Particles dispersed in an electrolyte solution are usually surrounded by diffuse electric double layers. If they approach each other, the double layers overlap and particles repel each other as discussed in Chapt. 10. Thus, the significant properties of the interactions are the ζ -potentials and the thickness of the double layers (the inverse of the Debye-Hückel screening parameter, Eq. 10.19). The ζ -potentials are measured in terms of electrokinetic phenomena (see Sec. 10.5).

The electrostatic repulsive interactions between charged spheres are discussed in Sec. 10.4. The attractive dispersion forces have been treated in Chapt. 8. As shown in Eq. 10.44, the total interaction free energy is given by

$$\Delta G_T = \Delta G_R + \Delta G_A + \Delta G_S \quad (11.1)$$

In the DLVO theory, however, the solvent mediated term, ΔG_S , is ignored.

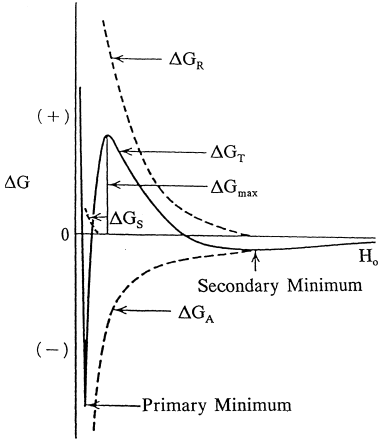


Fig. 11.1 The behavior of ΔG_T as a function of H_0 .

As an example, we consider interacting two identical spheres at a closest approach of H_0 . By using Eq. 8.13 or the dispersion forces in Table 8.1 and Eq. 10.53, the total interaction energy is given by

$$\Delta G_T = -\frac{A_{131}a}{12H_0} + \frac{64n^0k_B T}{\kappa^2} \pi a \gamma^2 e^{-\kappa H_0} \quad (11.2)$$

where a is the radius of the spheres and $\gamma = \tanh(ze\psi_0/4k_B T)$, ψ_0 being the potential at the surface of the spheres, and A_{131} is the Hamaker constant. The constant is given by Eq. 8.12 or obtained from Eq. 8.39, in which $D(\omega)$ corresponds to the secular equation found from the Green differential equation, Eq. 8.37, under appropriate boundary conditions.

The general behavior of ΔG_T relative to the distance, H_0 , is depicted in Fig. 11.1. When two particles come to contact, there is sometimes a strong repulsion, called Born repulsion due to the overlapping of atomic electron clouds, causing the primary minimum. The particle coagulation occurs at this distance of the primary minimum. The height of the potential barrier, $\Delta G_{T,\max}$, which opposes the coagulation, is proportional to the particle size. Thus, the smaller the particle size is, the harder it is to stabilize the dispersion. For larger electrolyte concentrations, ΔG_R and this height decrease and the coagulation can easily occur.

The behavior of the free energy for interacting two flat surfaces is the same as that for two spheres.

The concentration for which the height of ΔG_T is zero is called the critical coagulation concentration (CCC). It occurs when both $\Delta G_T = 0$ and $d(\Delta G_T)/dH_0 = 0$ are satisfied. Namely, we find from Eq. 11.2 that both vanish at $\kappa H_0 = 1$, so that

$$CCC \text{ (molecules/cm}^3\text{)} = \frac{9.85 \cdot 10^4 (\epsilon_0 \epsilon)^3 (k_B T)^5 \gamma^4}{A_{131}^2 (ze)^6} \quad (11.3)$$

For interacting two flat surfaces, the CCC occurs when $\kappa H_0 = 2$.

For a large ψ_0 , $\gamma \sim 1$. Then, the CCC is inversely proportional to the sixth power of the ionic valency. Thus, the value of the CCC strongly depends on the valency, which has been known empirically as the Schulze-Hardy rule. The inverse sixth power law as well as the decrease of $\Delta G_{T,\max}$ with concentrations are experimentally well verified. These are successfully explained by the DLVO theory.

However, Eq. 11.3 shows that, for a small ψ_0 , the value of the CCC is inversely proportional to the square of the valence, i.e.,

$$CCC \text{ (molecules/cm}^3\text{)} = \frac{385(\epsilon_0 e)^3 k_B T \psi_0^4}{A_{131}(ze)^2} \quad (11.4)$$

This gives the relation, $\psi_0^2/\kappa = \text{constant} \cdot A_{131}$, which seems to correspond to the empirical Eilers-Korff relation, $\psi_0^2/\kappa = \text{constant}$.

In colloidal particles, the values of ψ_0 are usually not so large. Nevertheless, the inverse sixth power law sometimes holds. In some cases, the CCC is proportional to z^{-4} . In order to explain these phenomena, there are various models by introducing a Stern layer (Overbeek, 1980; Israelachvili, 1985), by treating the surface charge (Honig and Mul, 1971; Metcalfe and Healy, 1990), and by considering the coagulation rate (Frens and Heuts, 1988).

In Fig. 11.1, the shallow secondary minimum is observed in the profile of ΔG_T at $H_0 = 15\text{--}25$ nm. This minimum is deeper for larger spheres or plate-like particles, which have a large mutually facing area and the larger attractive force. If it is deeper than several times $k_B T$, particles can be trapped in this minimum to cause flocculation on collision. The nature of flocculation in the secondary minimum differs from the coagulation in the primary minimum in that the floc is easily dispersed. This property has been experimentally proved by Hachisu and Furusawa (1963) and is practically used in paints, where a loosely flocculated structure entails a yield point. Thus, it prevents running and dripping during application and also prevents a hard sediment from forming in time at the bottom of the can.

The DLVO theory has also been proved in its validity in the stability of soap films (Scheludko, 1966) and in the direct DLVO force measurements between two mica surfaces (Claesson et al., 1984) as well as between two sapphire surfaces (Horn et al., 1988).

However, as Matijevic showed in 1973, the effect of electrolytes on the stability of dispersions in aqueous media is not fully described unless the possibility of complex ion formation is included. Complex ions change the ionic strength of the medium and they can change the charge on the particle by adsorption.

11.2 Kinetics of Coagulation

If the system is monodisperse, the coagulation may be called the homocoagulation. Otherwise, it is called the heterocoagulation.

11.2.1 Homocoagulation

This subject has been discussed by Russel et al. (1989) in terms of statistical mechanics. Particles undergo Brownian motion. In particular, when two particles approach and coagulate one another, the hydrodynamic interactions can be significant as described in Sec. 4.1.3. For a dilute system, the hydrodynamic interactions can be considered only for two approaching particles. In the following, we consider the coagulation kinetics in an intuitive fashion.

For a monodisperse system, if coagulation occurs it is not monodisperse any more. Ignoring this, the rate of change of the number density, n^0 , of spherical particles in the bulk is given by

$$\frac{dn^0}{dt} = -k(n^0)^2 \quad (11.5)$$

where k is the rate constant for forming two-particle clusters. If large clusters thus formed are to be included, the rate equation must be accordingly modified (Exercise 11.3 and Sec. 11.2.2). The solution of Eq. 11.5 is easily obtained as

$$1/n^0 = 1/n_0 + kt \quad (11.6)$$

where n_0 is the initial number density in the bulk.

Now let us evaluate k from the properties of the disperse system. The particles are in Brownian motion and approach each other by diffusion and by overcoming the potential barrier (against the interparticle force). Thus, we must use the discussion developed in Sec. 4.1.3. The rate, J , of particles radially crossing the spherical surface of radius r surrounding any particle is given by

$$J = 4\pi r^2 n v_{av} \quad (11.7)$$

where n is the number density of the particles at r and v_{av} is the average of their inward radial drift speed. This drift speed can be given by the mobility times the inward forces acting on the particle: the effective Brownian inward force, $d/dr(k_B T \ln n)$, plus the mechanical inward force due to the interparticle potential, $d\Delta G_T/dr$. Here, since the mobility is for the relative radial motion, it is two times b_{11} of Eq. 4.79, so that the mobility $= A_{11}/3\pi\eta a$ (see also Eq. 4.85 for the relative diffusion coefficient), where $A_{11} = 1 - (15/4)(a/r)^4$, which smoothly connects to

$0.775-2(2-r/a)$ as $r \rightarrow 2a$. (This A_{11} is not a Hamaker constant.) Then, Eq. 11.7 can be written as

$$J = \frac{4k_B T}{3\eta a} r^2 A_{11} e^{\frac{-\Delta G_T}{k_B T}} \frac{d}{dr} \left(n e^{\frac{\Delta G_T}{k_B T}} \right) \quad (11.8)$$

If the particles do not coagulate each other while approaching the central particle, the conservation of singlet particles holds and J is constant. Therefore, if we assume the boundary conditions:

$$\text{at } r = 2a, \quad n = 0 \text{ (coagulation occurs)}$$

$$\text{as } r \rightarrow \infty, \quad n = n^0 \text{ (in the bulk)} \quad \text{and} \quad \Delta G_T = 0$$

we have

$$J = \frac{4k_B T}{3\eta a} \frac{n^0}{\int_{2a}^{\infty} e^{\frac{\Delta G_T}{k_B T}} \frac{dr}{r^2 A_{11}}} \quad (11.9)$$

J is now the number of particles approaching the central particle per unit time. This is the rate of binary collisions with the single central particle and two single particles are lost at each collision from the group of uncoagulated particles. Since there are n^0 such central particles at time, t , the total number of collisions per unit time is $Jn^0/2$, where the division by 2 avoids the double counting. Since two single particles are lost at each collision, the rate of change of the total number density of the uncoagulated particles in the bulk at t is given by

$$\frac{dn^0}{dt} = -Jn^0 \quad (11.10)$$

Comparing with Eq. 11.5 under the present approximation, the rate constant k is given by

$$k = J/n^0 \quad (11.11)$$

Using Eq. 11.6, the half-life is given by

$$t_{1/2} = \frac{1}{kn_0} = \frac{3\eta a}{4k_B T} \int_{2a}^{\infty} e^{\frac{\Delta G_T}{k_B T}} \frac{dr}{r^2 A_{11}} \frac{1}{n_0} \quad (11.12)$$

This half-life may be used to experimentally determine the numerator (interparticle force) (Exercise 11.3).

If $\Delta G_T = 0$ except for $r = 2a$, where the potential is strongly negative, the coagulation is called the rapid coagulation, standing for no interactions. Otherwise, it is called the slow coagulation. Since $A_{11} \sim 1$, from Eq. 11.9 the flux for the rapid coagulation is given by

$$\begin{aligned} J_0 &= (8k_B T / 3\eta) n^0 \\ &= 1.2 \cdot 10^{-11} n^0 \text{ s}^{-1} \text{ for water at } 25^\circ\text{C} \end{aligned} \quad (11.13)$$

This is the number of binary collisions per unit time with a given central particle. The ratio J_0/J is called the stability ratio and, usually, denoted by W .

$$W = \frac{J_0}{J} = 2a \int_{2a}^{\infty} e^{\frac{\Delta G_T}{k_B T}} \frac{dr}{r^2 A_{11}} \quad (11.14)$$

In evaluating the integral of Eq. 11.14, we approximate $\Delta G_T(r)$ of Eq. 11.2 by expanding it around its maximum r_{\max} . We write

$$\Delta G_T = G_{\max} + \frac{1}{2} \left(\frac{d^2 \Delta G_T(r)}{dr^2} \right)_{\max} (r - r_{\max})^2$$

Substituting this into the above equation, we have approximately

$$W = \frac{2a}{r_{\max}^2} \int_0^{\infty} \exp(-p^2 x^2) dx, \quad p^2 = - \left(\frac{d^2 \Delta G_T(r)}{dr^2} \right)_{\max} / k_B T$$

Note that p is positive since the point of evaluation corresponds to maximum. The value of the last integral is then $\pi^{1/2}/(2p)$. Noting Eq. 11.2, G_{\max} and p may be evaluated and we find

$$\log_{10} W = -k_1 \log_{10} c + k_2 \quad (11.15)$$

where c is the electrolyte concentration ($k_1 = A_{131} a / 24 r_{\max} k_B T$). The value of W can be determined by turbidity and this relation is experimentally verified (Miller and Neogi, 1985). Although k_1 is theoretically obtained as

$$k_1 = 2.0 \cdot 10^7 a \gamma^2 / z^2 \text{ for aqueous solutions at } 25^\circ\text{C},$$

this relation with respect to a and γ has not been experimentally confirmed (Kihara et al., 1992).

11.2.2 Heterocoagulation

Coagulation of unlike particles is called heterocoagulation. Eq. 10.56 describes the repulsive interaction energy between two spheres with different sizes at the same surface potential. If the surface potentials are, in addition, different, Wiese and Healy (1970) used Eq. 10.46 and the Derjaguin approximation and gave

$$\Delta G_R(H_0) = \frac{\pi\epsilon_0\epsilon a_1 a_2}{a_1 + a_2} \left[2\psi_{01}\psi_{02} \ln \frac{1 + e^{-\kappa H_0}}{1 - e^{-\kappa H_0}} \pm (\psi_{01}^2 + \psi_{02}^2) \ln(1 - e^{-2\kappa H_0}) \right] \quad (11.16)$$

where the surface potentials refer to those at an infinite separation and the double sign, + or -, stands for the constant potential or the constant charge, respectively. If the particle size is too small for the approximation, use the expression given by Ohshima et al. (1983). Equation 11.16 can possibly be used for the constant potential model if the potentials are lower than about 50 mV. But this equation cannot be used for $\psi_{01} = \psi_{02}$. For higher approximation, see Ohshima et al. (1982). In the constant charge model, the linear approximation used to derive Eq. 11.16 is not so good for shorter distances of the particles and must be replaced by a more rigorous treatment (Gregory, 1975). If soft particles are involved, see Ohshima (1994).

An interesting feature of Eq. 11.16 is that, for constant potential, the interaction is attractive for all separations if the surface potentials have different signs, but is repulsive at large distances and becomes attractive within a certain distance if the surface potentials have the same sign but different values (Exercise 11.7). For constant charge, the interaction is repulsive in all separations if the potentials have the same sign, but is attractive for large distances and repulsive within a certain distance if the potentials have different signs.

From Eq. 10.57, the dispersion interaction energy is given by

$$\Delta G_A(H_0) = -\frac{a_1 a_2 A_{132}}{6(a_1 + a_2)H_0} \quad (11.17)$$

From Eq. 8.12, $A_{132} = A_{12} + A_{33} - (A_{13} + A_{23})$, where A_{12} , etc. are the Hamaker constants in vacuum. Using Eq. 8.10, we can write

$$A_{132} = (A_{11}^{1/2} - A_{33}^{1/2})(A_{22}^{1/2} - A_{33}^{1/2}) \quad (11.18)$$

A_{132} is negative if, for instance, $A_{11} > A_{33} > A_{22}$. Therefore, the dispersion force can be repulsive. On the other hand, the dispersion force between identical particles is always attractive, since

$$A_{131} = (A_{11}^{1/2} - A_{33}^{1/2})^2 > 0, \text{ always} \quad (11.19)$$

When the Hamaker constant is negative, in contrast to usual cases, a particle coagulation occurs at lower concentrations of an electrolyte but it becomes dispersed at higher concentrations. As an example, the Hamaker constant between a Hg droplet and an air bubble is negative ($-7.2 \cdot 10^{-20}$ J) in water and they are dispersed when the concentration of an electrolyte (KF) is increased (Usui et al., 1986). This property has a wide application in industry, including attachment or separation between colloidal particles and fibers (Tamai et al., 1980) and between colloidal particles and quartz surface (Tagawa, 1986) in washing. Attachment between particles and bubbles is one of the most important processes in ore flotation and it is investigated an application of heterocoagulation (Nishimura et al., 1990). Heterocoagulation is also studied for formation of complex particles (Furusawa and Anzai, 1992).

The stability ratio of the mixed system, W_t , of particle 1 and particle 2 is given by (Hogg et al., 1966)

$$\frac{1}{W_t} = \frac{n_1^2}{W_{11}} + \frac{n_2^2}{W_{22}} + \frac{2n_1n_2}{W_{12}} \quad (11.20)$$

where W_{11} and W_{22} are the stability ratio of homocoagulation of particle 1 and that of particle 2, respectively. W_{12} is the stability ratio of heterocoagulation of the two particles and n_1 and n_2 are the fractions in the dispersion ($n_1+n_2=1$). There are many experimental confirmations of Eq. 11.20 (see, for instance, Sasaki et al. (1980)).

11.3 Polymer or Steric Stabilization of Dispersions

Stabilization of dispersions by polymers has been widely investigated in industry (paints, glues, inks, medicine, food, detergents, lubricants, etc.). It has many advantages compared to electrostatic stabilization. First of all, polymer stabilization is insensitive to electrolytes. It works in aqueous as well as in non-aqueous media and in any particle concentration. In addition, if flocculation occurs under polymer stabilization, it is reversible.

Of course, polymers can work as a coagulating agent, called polymeric flocculation. For instance, polyacrylamide, which has many positive charges, is used for coagulating negatively charged particles by simply neutralizing them (Gregory, 1983). Or, polymers can be adsorbed by more than one particle at a time, forming a polymer bridge (Ji et al., 1990).

There is a third type of attractive interaction between surfaces associated with polymers, called a depletion interaction. Suppose that two particles are immersed in a polymer solution. If the polymer is of a relatively large size, the solution between the mutually approaching particles is depleted with polymer and the osmot-

ic pressure results in the attractive force between them. The mechanism is understood as follows.

Polymers usually form random coils of an average radius, R_g (the radius of gyration defined in Eq. 6.12), due to Brownian motion of the segments. When the segment-segment interactions of the polymer are equal to the segment-solvent interactions (an ideal solvent or a theta solvent), the system is said to be in the theta state. In this state, R_g is given by, due to Flory (1969) (see Exercises 11.8 and 11.9)

$$R_g = \frac{l\sqrt{n}}{\sqrt{6}} = \frac{l\sqrt{M/M_0}}{\sqrt{6}} \quad (11.21)$$

where n is the number of segments in the polymer, l is the effective segment length, and M and M_0 are the molecular weight of the polymer and that of each segment ($M=nM_0$), respectively. If the solvent is a good solvent, the polymer expands with the Flory radius $R_F = \alpha R_g$ (the intermolecular expansion factor: $\alpha > 1$). But if it is a poor solvent it shrinks ($\alpha < 1$). The size is also affected by the surface density of polymers adsorbed or grafted on a particle.

Now, consider two surfaces in a dilute solution of polymer. If they approach each other closer than R_F , and if the polymer are not adsorbed on the surfaces, the polymers between them are pushed out from the gap resulting in a reduced polymer concentration between the surfaces. If the bulk polymer concentration is ρ , the solvation or osmotic pressure approaches a value given by $-\rho k_B T$. If this pressure is assumed to act uniformly over a distance of R_F , the depletion free energy per unit area is given by

$$\Delta G_{\text{depl}} \sim -\rho R_F k_B T \quad (11.22)$$

which leads to an attractive depletion force per unit area between the surface. This is usually small compared to the van der Waals force (Exercise 11.10), unless ρ is large (Evans and Needham, 1988). However, if the solvent is good, the reduction of the concentration between the facing surfaces does not occur, when they approach. Instead, they prevent their approaching closer than R_F and impart the stability. We must note that a solvent can be good or poor depending on temperature.

Steric stabilization is the word used for stabilization by polymers, each of which is firmly anchored to a particle surface to withstand shear forces. Although natural polymers can work, the most effective steric stabilizers are block or graft copolymers that contain anchoring group and stabilizing chains. The anchoring group is usually insoluble in the dispersion medium and has strong affinity for the particle surface. The stabilizing chain must have a strong affinity for the medium, so as to make the polymer-coated particles well dispersed in the medium. The anchoring of a polymer is best to occur only at a few points on the particle surface and the bulk of the polymer extends into the solvent as far as the size, R_F (Eq. 11.21), to participate in the stabilization. The anchoring will or will not be

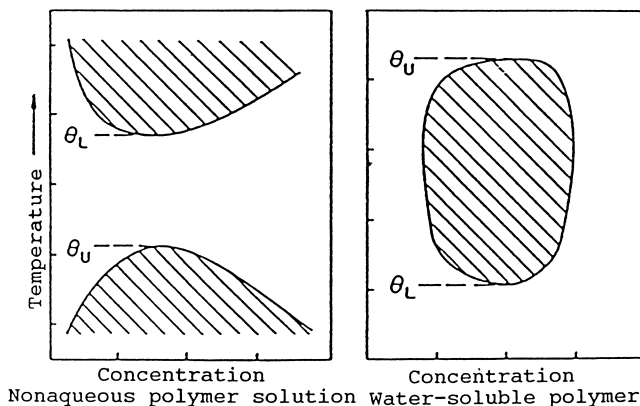


Fig. 11.2 Schematic phase diagram of a polymer of an infinite molecular weight in a solvent (Croucher, 1981, with permission from Academic Press). (The one-phase region is unhatched.)

reversible depending on the choice of polymer. A list of anchoring polymers is given by Napper (1983).

When two polymer-covered surfaces approach one another under Brownian motion, they experience a force once the outer chains begin to overlap. This interaction usually leads to a repulsive osmotic and entropic force. This is because the polymer chains interpenetrate at the encounter, whereby the chain concentration increases in the interaction zone by driving out solvent molecules into the bulk medium. The osmotic effects will then cause the medium to diffuse into this region and drive the surfaces apart. At the same time, the polymer chains are compressed by the increased concentration, leading to a reduction in the number of configuration they can adopt. Thus, the entropy is reduced, implying an increase of the free energy, which causes a repulsion. This repulsion is called steric or overlap repulsion.

The range of the steric interactions depends on the extension, R_F , of the polymer chains into the solvent. The minimum of the total interaction energy occurs at the location of the chains, not at the location of the primary minimum discussed before, provided the particles are well coated by polymers.

If flocculation occurs, it is not the result of overcoming of repulsion by particle-particle attraction, but, instead, due to the insolubility and precipitation of the stabilizing chain.

It is therefore understood that the steric stability strongly depends on the interactions between the polymer and the solvent. If the interactions are strongly attractive, the solvent is a good solvent for the polymers. But, otherwise, the phase separation of the solution occurs, leading to flocculation if particles are covered by the polymers. Therefore, the stability can be discussed in terms of the phase diagram of the solution (Fig. 11.2). The temperature at which the phase separation occurs is called the theta temperature of the polymer solution. More specifically speaking, in Fig. 11.2, the upper or lower theta temperature, θ_U or θ_L , lies at the

top or at the bottom of a two-phase (phase-separated) region, respectively. Since the polymers and the solvent molecules are electrically neutral, the interactions are the van der Waals dispersion interactions. The interaction energies are denoted by W_{11} for segment-segment, W_{33} for solvent-solvent, and W_{13} for polymer-solvent interactions, where the word “polymer” refers to the polymer segment and “solvent” to the solvent molecule. Then, according to a lattice model (Exercise 11.12), the change in the interaction energies among polymer segments and solvent molecules when mixed is proportional to the difference between W_{13} and the average $(W_{11}+W_{33})/2$.

$$\Delta W = W_{13} - (W_{11} + W_{33})/2 \quad (11.23)$$

Note that the approximation, $W_{13}=(W_{11}W_{33})^{1/2}$ (Eq. 8.9), cannot be used here, since polymer segments are covalently bonded to neighboring segments in contrast to the solvent molecules. Thus, since W 's are attractive (negative), the value of ΔW is negative if W_{13} is stronger than the average of W_{11} and W_{33} . In this case, polymers repel each other. But if W_{13} is weaker, ΔW is positive and polymers attract each other. The thermodynamical behavior of the polymers may be analogous to a van der Waals gas.

Consider the van der Waals equation of state, which is given by $(p+a/V^2)(V-b)=k_B T$ for one gas molecule (particle). It is known that b is related to the molecular volume of the particle and a (usually positive) is to the attractive interactions among particles. Thus, b affects the free or excluded volume of the gas molecules and, accordingly, the configurational entropy (Exercise 11.13). On the other hand, the constant, a , causes a pressure difference from the ideal case because of the interactions among particles, related to the enthalpic effect. (As seen in Eqs. 2.48, 2.50, and 2.55, b and a affect the number density and the activity coefficient, f , respectively.) They are combined in the second virial coefficient of the gas, as $B=b-a/k_B T$. If $B=0$, the gas behaves ideally ignoring the higher virial coefficients. If the gas molecules strongly attract each other, $B<0$ and they may stick together at Brownian encounters. If they strongly repel each other, $B>0$.

In analogy to the enthalpic term, $a/k_B T$, of the van der Waals B coefficient, the Flory parameter, χ , is defined for the polymer solution, by using the interaction energy change in mixing, ΔW , as

$$\chi = \left[W_{13} - \frac{1}{2}(W_{11} + W_{33}) \right] z / k_B T \quad (11.24)$$

where z is the number of nearest neighbors of segments or solvent molecules in solution (Exercise 11.12). In terms of χ , the second virial coefficient of the osmotic pressure of the polymer solution is given by (Hiemenz, 1986, p. 141)

$$B = \frac{\frac{1}{2} - \chi}{v_3} \left(\frac{v_1}{m_1} \right)^2 \quad (11.25)$$

where v_1 and v_3 are partial volumes of the polymer segment and the solvent molecule, respectively, and m_1 is the mass of the segment. In Eq. 11.25, the “1/2” term corresponds to the entropy of mixing, for instance, coming from the second term of the expansion: $k_B T \ln \varphi_3 = k_B \ln (1 - \varphi_1) = -k_B (\varphi_1 + 1/2 \varphi_1^2 + \dots)$, φ_1 and φ_3 being the volume fractions of the polymer segments and the solvent molecules, respectively. Like in the van der Waals gas, the coefficient, B , is an important quantity for judging the condition of a polymer solution. Namely, the theta condition, strictly speaking, corresponds to $B=0$. The solvent is good ($\alpha > 1$) if $B > 0$ and poor ($\alpha < 1$) if $B < 0$. The phase separation will occur for $B < 0$. This condition can be, however, easily changed, for instance, by changing the temperature or by varying concentrations.

The value of χ is known to depend on the concentration of polymers (see Eq. 13.46). It is understandable that if the volume fraction of polymers is very close to unity the amount of solvent is too small to fully interact with polymers. The result is that the solvent behaves as a poor solvent, as experimentally shown by Hökeš et al. (1971).

In particle dispersions, the Flory-Huggins theory (Flory, 1941; Huggins, 1941) predicts that if $B > 0$ there is a steric repulsion among polymer-covered particles, while if $B < 0$ steric effects contribute an additional attractive term, leading to the phase separation (flocculation). The temperature corresponding to the conditions that $B=0$ is the critical flocculation temperature. In reality, however, other factors can upset this simple prediction, especially when the surface-segment attraction energy is large or when excitations in the rotational and vibrational states of the polymers are induced by changing temperatures, so that ΔW depends on T . At lower temperatures, polymer segments are not so free as considered in the theory. At higher temperatures, solvent molecules are more violently moving but the segments of each polymer are still not so free.

It is known (de Gennes, 1987) that theories of steric interactions are complex. The forces are known to be strongly affected by the quality of the solvent, but they also depend on the quantity or coverage of polymer on each surface and on whether the polymer is simply adsorbed from solution (a reversible process) or irreversibly grafts onto the surfaces. Scheutjens and Fleer (1979, 1985) introduced a semi-infinite number of sites near a surface and arranged, in various possible ways, polymer segments and solvent molecules among the sites under certain interactions to compute the partition function. Thus, they obtained the adsorption isotherm and the density distribution of the polymer segments. The results on the adsorption isotherm and segment density profile have been qualitatively verified with sodium polystyrene sulfonate by the photon correlation technique and small-angle neutron scattering, respectively (Cosgrove et al., 1986). The lattice theory is extended to cover the adsorption of a polymer electrolyte by Cohen Stuart et al. (1991). Another approach is to develop a differential equation describing the chain configurations, a mean-field approximation for the segment-segment interactions and interactions with surfaces, and the Derjaguin approximation to convert results for flat plates to geometries with curvature (see Takahashi and Kawaguchi, 1982; Napper, 1983; Gast and Leibler, 1986; Russel et al., 1989). For interactions in poor and theta solvent are the theories sufficiently well developed by Ingersent et al. (1986, 1990).

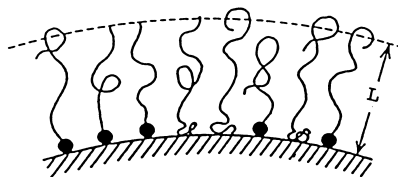


Fig. 11.3 A polymer brush.

When polymer coverage is high, polymer chains are forced to extend away from the surface much farther than R_g . As an example, the steric repulsion has been calculated for the simplest case of end-grafted chain polymers (Fig. 11.3) on flat surfaces. The polymer layer is called a polymer brush. If the mean distance between attachment points is denoted by s , the thickness of the brush in a good solvent is given by (Alexander, 1977)

$$L = \frac{nl^{5/3}}{s^{2/3}} \quad (11.26)$$

where n is the number of segments with the effective segment length, l , of the polymer. (Recently, Kumacheva et al. (1993) investigated the physical nature of the polymer brush.) The segment density in the brush decreases as departing away from the surface and the repulsive energy exponentially decreases as the distance, H , between the surfaces. More exactly, if H is between $0.4L$ and $1.8L$, according to Alexander-de Gennes theory (de Gennes, 1985, 1987), the repulsive potential energy per unit area is given by

$$W(H) \approx \frac{100L}{\pi s^3} k_B T e^{-\pi H/L} \quad (11.27)$$

A different and complex expression for the force is predicted by Milner et al. (1988), which gives similar values as above. The Derjaguin approximation, Eq. 10.52, may be used to find the repulsive force between two polymer-covered spheres (Exercise 11.14). Patel and Tirrell (1989) expanded Eq. 11.27 to treat the interactions of block polymers under various configurations.

There are many ways of experimentally observing the dynamics of adsorbed polymer layers, such as small angle neutron scattering, neutron and x-ray reflectivity, NMR, ellipsometry, internal reflection spectroscopy, and various scattering techniques (Takahashi and Kawaguchi, 1982; Cosgrove, 1990). Flocculation strongly affects the light turbidity. In particular, the surface force can be measured by the surface force apparatus (SFA) at the Ångström level (Israelachvili and McGuiggan, 1990), which can also be used for opaque materials. The experimental results obtained by Taunton et al. (1990) for the forces between two end-grafted polystyrene brushes in toluene agree surprisingly well with Eq. 11.27. However, things usually are more complicated. First of all, many polymers do not have specific anchoring groups. In fact, each segment can bind to the surface with much weaker forces. Such adsorbed layers are highly dynamic, with individual

segments continually attaching and detaching from the surfaces. Indeed, the force between two surfaces can take many hours to reach its equilibrium and measured force profiles are often very hysteretic irreversibly on approach and separation. In addition, as time goes on, the attractive bridging component can be reduced, as observed by Luckham and Klein (1990).

When polymers are concentrated within an adsorbed surface layer their molecular relaxation times can be many times longer than in the bulk. Molecules, when concentrated, even freeze at the surfaces (Van Alsten and Granick, 1990). Thus, measured force laws could hardly refer to thermodynamic equilibrium.

Phenomenologically, polymers are soluble to form one phase or insoluble to form two phases, depending on the temperature, pressure, and additives to the dispersion medium. All these effects are results of chemical nature of polymer segments and solvent molecules as well as the volume change. The rates of changes of the volumes of polymers and solvent molecules with temperature are usually different. The critical flocculation point does not depend on the molecular weight of the polymers. However, the steric repulsive force depends on the thickness and density of the surface layer.

The temperature dependence of the steric stability provides a clue to the thermodynamic factors that control stability. As mentioned before, Croucher and Hair (1981) speculated a phase diagram, Fig. 11.2, of a polymer of infinite molecular weight in solution, including a nonaqueous polymer solution and a water-soluble polymer. There are, although not necessarily accessible for measurement, generally two (upper and lower) theta temperatures for each polymer concentration. In principle, in dilute dispersions, sterical stabilization will exhibit a critical flocculation temperature in each case of heating and cooling. The critical flocculation temperatures qualitatively correspond to the theta temperatures. But, the flocculation temperatures are rather insensitive to concentrations, although the theta temperatures depend on concentrations. The “upper” critical flocculation temperature (*UCFT*) is defined if the flocculation occurs on heating. The “lower” one (*LCFT*) is found if it occurs on cooling. The region of stability is between *LCFT* and *UCFT* for nonaqueous suspensions and the regions above *LCFT* and below *UCFT* for aqueous suspensions. It has been considered, in either a nonaqueous or aqueous dispersion, that flocculation at the *LCFT* occurs due to the difference in chemical nature between the steric stabilizer and the dispersion medium (the stabilization is entropic). Flocculation at the *UCFT* is controlled by the difference in size and flexibility between the steric stabilizer and the dispersion medium (the stabilization is enthalpic).

11.4 Stability of Liquid Droplets in Liquid (Emulsion)

The dispersion of liquid droplets in an immiscible liquid is an emulsion. The two immiscible liquids are represented by oil and water. Oil droplets can be dispersed in water (O/W) or water droplets in oil (W/O). In some cases, oil droplets which

hold water inside are observed to be dispersed in water (W/O/W) (Matsumoto, 1983) or the type (O/W/O) of emulsion has been reported (Matsumoto and Kang, 1989).

Stable emulsions require the presence of a third component (the emulsifying agent or emulsifier, see Sec. 1.3), but practical emulsions seldom consist of only three components. Polycomponent systems cannot be easily theoretically handled, so that the understanding of emulsions is largely empirical. When emulsions separate to two phases, the process is said to be “broken”. Because a density difference may exist between the two phases, the dispersed droplets may rise or sink within the medium by gravity or centrifuging; these processes are called “creaming” or “settling” (or “sedimentation”) and not related to the emulsion stability.

When two droplets coalesce at constant volume, temperature, and compositions, the free energy changes (Helmholtz) because the total area, A , decreases. From Eq. 2.10, we have

$$\Delta F = \gamma(A_{\text{final}} - A_{\text{initial}}) < 0 \quad (11.28)$$

where γ is the interfacial tension (positive). Thus, the coalescence is spontaneous. This instability of an emulsion can be observed by droplet counting under a microscope (Boyd et al., 1972), correcting for the possible sedimentation under gravity. Another interesting method is to use a Coulter counter (see Sec. 6.6). The kinetics of the coalescence is similar to that of homocoagulation (see Sec. 11.2.1). As shown below, the process is fairly rapid in the time scale required for the stability.

In order to improve the stability additional terms are required to make ΔF positive in Eq. 11.28. The change of the total area in Eq. 11.28 cannot be controlled. Therefore, the possible terms must include a third component, which is spontaneously adsorbed at the interface. If the total area is reduced and if some of the component will be removed from the interface, then the removal requires an energy, making the net ΔF positive. If the component stays at the interface, the increased surface density of the component will reduce the surface tension (Eq. 2.24 noting that $\pi = \gamma_0 - \gamma$), resulting in that the net ΔF is positive. Such a third component is called an emulsifying agent (see Sec. 1.3).

Effective resistance to coalescence of emulsion droplets is also conferred by certain finely divided solid particles. If the solid is preferentially wetted by one of the phases, then the solid particles promote an emulsion. Consider the solid particles are spheres of radius a , which sits at the flat interface between liquid 1 and 2 (Fig. 11.4). The contact area of the particle immersed in liquid 1 and the interfacial tension are denoted by A_{1p} and γ_{1p} , respectively. The corresponding quantities with liquid 2 are denoted by A_{2p} and γ_{2p} . Those between liquid 1 and 2 are given by A_{12} and γ_{12} . Ignoring gravity the equilibrium position of the particle is then determined by

$$\Delta F = \gamma_{1p}\Delta A_{1p} + \gamma_{2p}\Delta A_{2p} + \gamma_{12}\Delta A_{12} = 0 \quad (11.29)$$

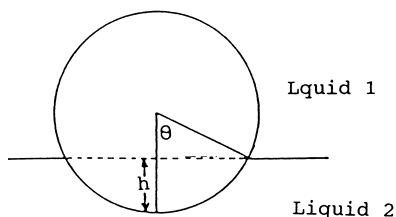


Fig. 11.4 A solid sphere at the interface.

A simple calculation gives (Exercise 11.15)

$$\gamma_{2p} - \gamma_{1p} = \gamma_{12}(1 - h/a), \quad 0 < h < 2a \quad (11.30)$$

where h is the distance between the flat interface and point O on the particle surface in contact with liquid 2 (Fig. 11.4). Therefore, if $\gamma_{2p} > \gamma_{1p}$, $h < a$ and the solid particle has a larger contact area with liquid 1. This is the position of the solid particle with respect to the flat interface corresponding to the minimum free energy. In this geometry, more solid particles can be found at the interface if liquid 2 forms a droplet in the medium of liquid 1, i.e., if the interface between liquids, 1 and 2, is convex toward liquid 1. This configuration stands for a less free energy and the stability against coalescence at Brownian encounters is similar to the steric stability of polymer-covered solid particles (see Sec. 11.3).

The kinetics of coalescence of emulsion droplets is mathematically similar to that of coagulation (see Sec. 11.2). At the time of coalescence, the shapes of the interfaces of the droplets must deform temporarily through energetically unfavorable shapes. The potential energy temporarily then increases and must be overcome in the process of coalescence. (The behavior of macroscopic (millimeter) droplets at the Brownian encounter has been photographed by a high-speed camera (Charles and Mason, 1960).) The energy to be overcome at the union is called the activation energy, ΔG_{Act} . In addition, dispersed liquid droplets are usually found to carry electric charges. If so, the interaction of two droplets obeys Eq. 11.2 or the like and must be included in the activation energy. Another complication will come from the repulsive hydration forces when water molecules bind strongly to hydrophilic groups (Rand and Parsegian, 1989; Furusawa et al., 1993). These forces, however, are not well understood.

For simplicity, assume that all of the droplets have the same radius, a . Then, Eq. 11.12 gives the time required for the number density of the droplets to be reduced to half of its initial value, n_0 . If ΔG_{Act} occurs within a very narrow region near the surfaces, instead of spreading over some distance, and $A_{11} = 1$, we have

$$t_{1/2} = \frac{3\eta}{8k_B T} e^{\frac{\Delta G_{\text{Act}}}{k_B T}} \frac{1}{n_0} \quad (11.31)$$

If $\Delta G_{\text{Act}} = 0$ and $n_0 = 10^{10}$ droplets/cm³, $t_{1/2}$ is about 20 s at 25°C. The lifetime of the emulsion is thus very short. Equation 11.31 tells that the lifetime is con-

trolled by ΔG_{Act} and the viscosity of the liquid medium. This equation does not show the dependence on the size of the droplets, so that the process of coalescence may be better treated in terms of the average volume of the dispersed droplets instead of the number of droplets. If the total volume of the dispersed phase per unit volume of the emulsion is denoted by V_T , the average volume of the droplets is given by $V_A = V_T/n^0$ in the bulk. Equation 11.10 can then be written as, in the approximation of Eq. 11.31,

$$\frac{dV_A}{dt} = \frac{8k_B T}{3\eta} V_T e^{-\frac{\Delta G_{\text{Act}}}{k_B T}} \quad (11.32)$$

Thus, since V_T is constant, V_A increases linearly with t . Experimentally, this linearity was confirmed by Lawrence and Mill (1954) with oil droplets emulsified by 1% sodium oleate in water and the value of $\Delta G_{\text{Act}} \sim 11 k_B T$ was obtained. This corresponds to the half-life of about 60 days.

Associated with Eqs. 11.31 and 11.32, we must note that the viscosity depends on the concentrations (Eqs. 4.29 a, b, and c), the shape of the particles (Eqs. 4.22a, b, and 4.23), and the internal circulation in the droplets (Eq. 4.21). If emulsions are charged, the viscosity is affected. But the effect is small at low ζ -potential (< 100 mV), high electrolyte concentrations ($> 10^{-2}$ M), or large particle size (> 25 nm) (Vold and Vold, 1983). In addition, the apparent viscosity increases or decreases as the rate of shear increases and these phenomena may be time-dependent (Tanner, 1985).

Most emulsions are less stable at higher temperatures, because the adsorption of the stabilizer decreases with temperature. In some cases the emulsifying agent is thermally decomposed. O/W emulsions stabilized electrostatically without protective colloid are subject to breaking on freeze-thaw cycling. The separation of ice allows the electrolyte in the aqueous medium to become concentrated, thus reducing the electrostatic repulsion between droplets. This increase of concentrations can be accomplished by the addition of electrolyte, such as a salt with multivalent ions, whereby the emulsion is destabilized.

Emulsions will break if the emulsifying agents are chemically altered by, say, adding acid or metal ions. The emulsifying agent can be desorbed from the droplets by adding a water-soluble organic solvent, such as methanol, ethanol, or acetone, to an O/W emulsion or by the addition of an oil-soluble Lewis base or Lewis acid, whichever is effective. Similarly, emulsions which are stabilized with adsorbed solid particles can be broken by adding a solvent that wets the particles and removes them from the interface.

11.5 Stability of Aerosols

Aerosols such as fog, liquid spray, etc., are different from emulsions in that the dispersion medium is a gas. The mean free path λ of the gas molecules can be comparable to or less than the size a of the droplets or particles. The viscosity is then reduced due to the slippage of gas molecules along the particle surface. Thus, the Stokes law, Eq. 4.20, needs a correction (the Stokes-Cunningham correction), which affects the collision rate and, accordingly, the stability of aerosols. According to Davies (1943),

$$\eta = \eta_0 / [1 + Kn(1.257 + 0.400e^{-1.10/Kn})] \quad (11.33)$$

where Kn is the Knudsen number given by λ/a and η_0 stands for $Kn \rightarrow 0$. Otherwise, the coalescence of aerosols is similar to that of emulsions (Hidy and Brock, 1972), as discussed in Chapt. 14.

One of the practically important aspects with aerosols, smog, etc. is a process of particle capture or filtration. The theory is not fully developed (Spielman, 1977; Tien and Payatakes, 1979; Russel et al., 1989, p. 367).

11.6 Stability of Bubbles and Foams

A foam is a coarse dispersion of gas in liquid (or solid). There are two types: bubble foams and concentrated foams. The former are nearly spherical bubbles separated by a bulk liquid, while the latter are mostly polyhedral gas cells partitioned by thin films (some exceptions like in foam rubber, where foams are spherical).

The bubble formation is discussed in Chapt. 3 covering to the point of the critical size. (A further growth in size may be mathematically investigated by following Kielkiewicz (1993).) The bubbles will rise to the surface of the bulk liquid by gravity. The thinning of the upper bubble surface can be monitored by interference colors and its final profiles have been calculated (Platikanov, 1964). The bubbles may eventually be drained to form foams, like in a glass of beer.

Pure liquid do not form stable foams, with possible exceptions of thin films of liquid metals. In coalescence of foam cells, if the total surface area of the film decreases by ΔA (<0) at constant temperature, volume, and compositions, the change of the Helmholtz free energy is given by

$$\Delta F = \gamma \Delta A \quad (11.34)$$

where γ is the surface tension. Since $\Delta A < 0$, $\Delta F < 0$. Thus, like emulsions (Eq. 11.28), a foam composed of an insoluble gas in a pure liquid is thermodynamically stable.

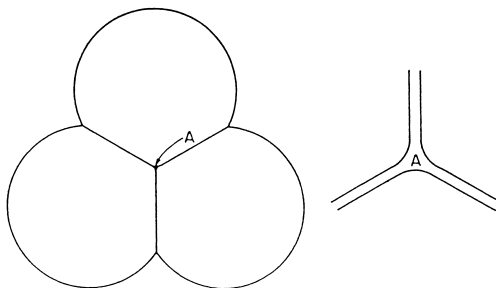


Fig. 11.5 Plateau's border: A
(Adamson, 1990, with permission
from Wiley).

mically unstable. In addition, foams allow film thinning by drainage (Exercises 11.16 and 11.17) as well as evaporation and entrained air to escape. Hence, certain solutes (foaming agents) are necessary to achieve stability by retarding the tendencies. Surely, foaming agents will behave in a different way from emulsifiers (see Sec. 11.4), although good emulsifiers are usually also good foaming agents.

If a surfactant forms a monolayer film covering a liquid, the rate of evaporation is reduced. In most of the studies, water was used for the liquid. Then, since the surfactant has a low solubility, the activity of water and, accordingly, the equilibrium vapor pressure are not affected by the presence of the monolayer film. But the rate of evaporation has been observed to depend on the length of the alkyl chain of *n*-alcohols (LaMer et al., 1964). The reduction of the rate can be as high as 90% at a higher film pressure. Barnes (1986) has reviewed this effect.

In order to observe the temporal behavior of foams, it must be retarded by using foaming agents. When foams are in contact with each other, they are partitioned by a continuous thin liquid film to a polyhedral shape. Some portions of the film surface are flat, where two bubbles meet, and others are curved, where more than two bubbles meet (Plateau border, Fig. 11.5). The pressure of the liquid inside the film is higher at the flat portion than at the curved portion due to the surface tension (Exercise 2.3). Hence, liquid in the flat portion of the film is kept to be drained to the curved portion. The flow drags some of the surface layer along with it, so that it locally creates a surface with less foaming agent and hence higher surface tension (the Gibbs effect). The diffusion of a foaming agent is slow if the concentration (gradient) is not high, and this higher tension promotes a counter flow. Namely, the higher tension exerts a pull on the adjacent areas of lower tension, causing the surface to flow toward the region of higher tension (the Marangoni effect), and the viscous drag of the moving surface carries liquid in the film with it. These effects occur almost simultaneously as complements to each other and thus affect foam stability. However, the film will be ultimately so thinned that the Marangoni effect cannot operate. Its thickness is molecular level size and molecules in the film lose the properties of the continuous bulk liquid. But, molecules are generally attractive each other, and favor film thinning. If the foaming agent is ionic, the overlapping of electric double layers near the both sides of the film surfaces gives repulsive forces (the DLVO theory) and opposes the film thinning. However, the film will eventually rupture, allowing a coalescence of foams.

The drainage has been observed by interference colors with a soap film stretched across a vertically positioned (glass or metal) frame in a closed system to avoid evaporation. For a thick film, hydrodynamics may be used for the study of drainage (Exercise 11.17). As drainage occurs due to gravity, the interference color changes across the film and eventually the top region takes on a silvery appearance and, then, black spots appear in the region and develop to black films. The theoretical treatment of these interference effects is complicated (Bikerman, 1953).

As film thinning continues, two types of black films are observed with apparently a stepwise transition in thickness (Overbeek, 1960). This indicates that the Gibbs energy as a function of the film thickness has two minima, standing for a metastable thickness each. In a soap film, a common (or first) black film appears first and then it develops to a more stable Newton (or second) black film. The thinnest (Newton) of these black films is 45 Å thick, about twice that of the soap monolayer. But some films may lose the stability and break before reaching this thickness. Uemura et al. (1985) observed by infrared absorption of OH vibrational frequency (3400 cm⁻¹) that the hydrocarbon portion of the surfactant lies outside of the aqueous core of the film. Likewise, Yamanaka et al. (1994) observed the effect of metal ions on the equilibrium thickness of foam films down to about 25 Å.

An important characteristic of stable films is their resistance to mechanical disturbance. The elasticity, E , of a surface has been introduced by Eq. 2.43. Since the surface pressure is $\pi = \gamma_0 - \gamma$ and the film has two surfaces, we have

$$E = 2 \frac{d\gamma}{d \ln A} \quad (11.35)$$

where A is the surface area. Here, A may be replaced by A_m , the surface area per molecule of the monolayer. Note also Eq. 2.26 for a two-component system. Eq. 11.35 can be rewritten as

$$E = (2n_2^0)^2 \frac{d\mu_2}{dn_2^0} \quad (11.36)$$

where μ_2 is the chemical potential of the monolayer species and from Eq. 2.24 $\Gamma_2^1 = n_2^s/A = n_2^0$, the number of molecules per unit area of the monolayer (Exercise 11.19), so that $A_m = 1/n_2^0$. E has values in the range of 10 to 40 dyne/cm (Prins and van den Tempel, 1969).

The above is the isothermal elasticity. If a film is compressed, the temperature of the film changes because of the entropy change, whereby the elasticity increases. Thus, the adiabatic elasticity is larger than above. Ternes and Berg (1984) discussed the importance of E . High elasticity and resilience are important to give a good foam stability, but high surface viscosity appears also to be important. This may be related with the film drainage (see Friberg et al., 1986).

Exercises

- 11.1** Find $\Delta G_{T,\max}$ from Eq. 11.2 and discuss the variation with the electrolyte concentrations.
- 11.2** Establish Eq. 11.3.
- 11.3** Consider a possible case of successive coagulations, so that k -mer clusters are formed ($k=2,3,\dots$). For simplicity, k -mer clusters, called particles of type k , are spherical with radius, a_k . We may approximate the total number of collisions, c_{ij} , per unit time between particles of type i with those of type j by

$$c_{ij} = 4\pi D_{ij} a_{ij} n_i n_j$$

where D_{ij} is the relative diffusion coefficient for the relative motion between a particle of type i and a particle of type j . The radius a_{ij} is the center-to-center distance between particles of type i and type j at collision, where the two particles coagulate one another and form a particle of type $i+j$. Set up the rate equation for the number density n_k of particles of type k . Note that particles of type k are produced by collisions of particle of type i with particles type j provided $i+j=k$ for all possible combinations of i and j . Note that n_k is reduced if particles of type k collide with any other particles.

- 11.4** Prove Eqs. 11.8 and 11.9.
- 11.5** Consider that, in Eq. 11.14,

$$\Delta G_T = -\infty, \quad r < 2a$$

$$\Delta G_T = G_{\max}, \quad 2a < r < 2a + 1/\kappa$$

$$\Delta G_T = 0, \quad r > 2a + 1/\kappa$$

Approximately evaluate W . Your result may be expressed as

$$W \sim \frac{1}{2\kappa a} \exp \frac{G_{\max}}{k_B T}$$

- 11.6** Establish Eq. 11.15.
- 11.7** In Eq. 11.16, plot the energy against κH_0 in the range of $\kappa H_0=0$ to 4 for the following two cases: (1) $\psi_{01}=10$ mV, $\psi_{02}=30$ mV and (2) $\psi_{01}=-10$ mV, $\psi_{02}=30$ mV.
- 11.8** Use Eq. 11.21, and find R_g if $l=1.0$ nm, $M_0=200$, and $M=10^6$. If we assume that the segment width is the same as the segment length l , what would be the real volume of the polymer? Then compare the volume with that of the sphere of radius, R_g . What fraction of this volume is occupied by the polymer volume? (Hint: Find the volume of the polymer from n ·(each segment volume), which is compared with $(4\pi/3)R_g^3$).
- 11.9** The diameter of a coiled linear polymer is crudely given by its rms end-to-end length, which for many carbon polymers is given by (following the random walk)

$$\langle r^2 \rangle^{1/2} = 0.06 M^{1/2} \text{ nm}$$

where M is the molecular weight. Compute the diameters for $M=10^6$, 10^5 , and 10^3 .

- 11.10** Calculate the depletion force between two spherical particles of radius a , assuming that the polymer coils are located just outside of the gap between two spheres. Evaluate the value when $\rho=10^{24} \text{ m}^{-3}$ and $R_g=5 \text{ nm}$ at 25°C . (Usually, this force is small compared to typical van der Waals' forces.)
- 11.11** Consider a polymer consisting of n segments, each of which has a length l , so that if it is fully extended the end-to-end length is nl . If the arrangement of segments obeys the random walk what is the end-to-end length? Ignore the self-avoiding nature. (Solution: If $W(h)$ denotes the probability that the end-to-end distance is between h and $h+dh$, $\sum W(h)4\pi h^2 dh = 1 \cdot \langle h^2 \rangle = nl^2$. Considering the random walk of n steps, we have

$$W(h)dh = \left(\frac{2\pi nl^2}{3}\right)^{-3/2} e^{-\frac{3h^2}{2nl^2}} dh$$

Then, the relation, $d\ln[4\pi h^2 W(h)]/dh=0$, gives the most probable value of $\langle h^2 \rangle = (2/3)nl^2$.

- 11.12** Referring to Eq. 11.23, consider a model for the polymer solution, which is a three-dimensional lattice of N sites of equal volume. The interacting neighbors of any one site is given by the number of nearest neighbors of any site, denoted by z . In the solution, there are N_1 polymers with n segments each and N_3 solvent molecules, and $N=nN_1+N_3$. We write $\phi_1=nN_1/N$ and $\phi_3=N_3/N$. Assume that the segments and the molecules have the same volume and the probability of occupying any unoccupied site of the N lattice sites is equal. Suppose that the lattice is initially separated to two of nN_1 and N_3 sites and the polymer segments and the solvent molecules initially completely fill separately those lattices, respectively. They are next mixed, so that any site is surrounded on the average by $z\phi_1$ segments and $z\phi_3$ solvent molecules and the central sites are occupied by either segments or solvent molecules. Show that the total change of the interaction energy between the initial and the mixed configuration is given by

$$W_i = \frac{1}{2} z N \phi_1 \phi_3 [2W_{12} - (W_{11} + W_{33})]$$

What is the interaction energy per segment or molecule?

- 11.13** Show that for a van der Waals gas

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + p \right] = \frac{k_B}{V-b}$$

- 11.14** Work out to find the steric repulsion between two spheres by using Eqs. 10.52 and 11.27.
- 11.15** Verify Eqs. 11.30 and 11.32.
- 11.16** Suppose that a thin film of liquid, 2, separates air, 1, into two semi-infinite regions. The van der Waals attractive interaction energy is given by $-A_{121}/(12\pi h^2)$ (Exercise 8.1), where A_{121} is the Hamaker constant and h is the film thickness. Use the approximation, Eq. 8.9, and show that $A_{121}>0$ and the interaction causes the film to thin and eventually burst in this continuous approximation.

- 11.17** While a foam film is thick, the Navier-Stokes equation may be used to analyze the slow drainage of the film due to a pressure gradient or gravity or both. Assume that the film surfaces are covered by a forming agent, so that the inner liquid of the film does not move at the surfaces (stick conditions). Find the thinning speed of the film spread across a vertical metal frame under gravity, assuming the flow speed of the liquid is slow. Because of the boundary condition, such drainage will correspond to a viscous flow between parallel plates. Gibbs' result (1931) shows that

$$v_{av} = \frac{\rho g \delta^2}{8\eta}$$

where the average velocity is given as a function of film thickness δ , liquid viscosity η , and density ρ . Derive this result. Assume that ρ is constant across the film.

- 11.18** Why is the film of the thickness much less than the all visible wavelengths called "black"?
11.19 Derive Eq. 11.36.
11.20 The equation of state of a spherical foam is given by (Morrison and Ross, 1983)

$$pV + \frac{2}{3}\gamma A = nk_B T$$

where p is the external pressure, V and A are the inside volume and the surface area of the spherical foam, respectively, and n is the number density of the gas molecules inside the foam. Suppose that two equal spherical foams coagulate to form a single spherical foam under a constant p and T . Use the above equation of state to find the V and A of the new foam.

References

- Adamson, A.W., "Physical Chemistry of Surfaces", 5th ed., John Wiley & Sons, Inc., New York (1990).
 Alexander, S.J., *Physique* 38, 983 (1977).
 Barnes, G.T., *Adv. Colloid & Interface Sci.* 25, 89 (1986).
 Bikerman, J.J., "Foams", Reinhold, New York (1953).
 Boyd, J., Parkinson, C., and Sherman, P., *J. Colloid Interface Sci.* 41, 359 (1972).
 Charles, G.E. and Mason, S.G., *J. Colloid Interface Sci.* 15, 195, 236 (1960).
 Claesson, P.M., Horn, R.G., and Pashley, R.M., *J. Colloid Interface Sci.* 100, 250 (1984).
 Cohen Stuart, M.A., Fleer, G.J., Lyklema, J., Norde, W., and Scheutjens, J.M.H.M., *Adv. Colloid Interface Sci.* 34, 477 (1991).
 Cosgrove, T., *J. Chem. Soc. Faraday Trans. I* 86, 1323 (1990).
 Cosgrove, T., Obey, T.M., and Vincent, B., *J. Colloid Interface Sci.* 111, 409 (1986).
 Croucher, M.D. and Hair, M.L., *J. Colloid Interface Sci.* 81, 257 (1981).
 Davies, C.N., *Proc. Phys. Soc. (London)* 15, 61 (1943).
 de Gennes, P.G., *C. R. Acad. Sci. (Paris)* 300, 839 (1985); *Adv. Colloid Interface Sci.* 27, 189 (1987).
 Evans, E. and Needham, D., *Macromolecules* 21, 1822 (1988).
 Flory, P.J., *J. Chem. Phys.* 9, 660 (1941).
 Flory, P.J., "Statistical Mechanics of Chain Molecules", J. Wiley, New York (1969).

- Frens, G. and Heuts, J.J.F.G., *Colloids Surf.* 30, 295 (1988).
- Friberg, S.E., Blute, I., and Kunieda, H., *Langmuir* 2, 659 (1986).
- Furusawa, K. and Anzai, C., *Colloids Surf.* 3, 103 (1992).
- Furusawa, K., Watanabe, K., and Matsumura, H., in "Food Hydrocolloids", eds. Nishinari, K. and Doi, E., Plenum Press, New York (1993).
- Gast, A.P. and Leibler, L., *Macromolecules* 19, 686 (1986).
- Gibbs, J.W., "Collected Works", Vol. 1, Longmans, Green, New York (1931).
- Gregory, J., *J. Colloid Interface Sci.* 51, 44 (1975).
- Gregory, J., in "Chemistry and Technology of Water Soluble Polymers", ed., Finch, C.A., Plenum, New York (1983), p. 307.
- Hachisu, S. and Furusawa, K., *Sci. Light* 12, 1, 157 (1963).
- Hidy, G.M. and Brock, J.R., "International Review of Aerosol Physics and Chemistry", Vol. 3, Pergamon Press, New York (1972).
- Hiemenz, P.C., "Principles of Colloid and Surface Chemistry", 2nd ed., Marcel Dekker, New York (1986).
- Hogg, R., Healy, T.W., and Fuerstenau, D.W., *J. Chem. Soc. Faraday Trans. I* 62, 1638 (1966).
- Höke, H., Shih, H., and Erman, B., *Trans. Faraday Soc.* 67, 2275 (1971).
- Honig, E.P. and Mul, P.M., *J. Colloid Interface Sci.* 36, 258 (1971).
- Horn, R.G., Clarke, D.R., and Clarkson, M.T., *J. Materials Res.* 3, 413 (1988).
- Huggins, M.L., *J. Chem. Phys.* 9, 440 (1941).
- Ingersent, K., Klein, J., and Pincus, P., *Macromolecules* 19, 1374 (1986); 23, 548 (1990).
- Israelachvili, J.N., *Chemica Scripta* 25, 7 (1985).
- Israelachvili, J.N. and McGuiggan, P.M., *J. Mater. Res.* 5(10), 2223 (1990).
- Ji, H., Hone, D., Princus, O.A., and Rossi, G., *Macromolecules* 23, 698 (1990).
- Kielkiewicz, M., *J. Aerosol Sci.* 24, 227 (1993).
- Kihara, H., Ryde, N., and Matijević, E., *J. Chem. Soc. Faraday Trans. I* 88, 2379 (1992).
- Kumacheva, E., Klein, J., Pincus, P., and Fetters, L.J., *Macromolecules* 26, 6477 (1993).
- LaMer, V.K., Healy, T.W., and Aylmore, L.A.G., *J. Colloid Sci.* 19, 676 (1964).
- Lawrence, A.S.C. and Mill, O.S., *Discuss. Faraday Soc.* 18, 98 (1954).
- Luckham, P. and Klein, J., *J. Chem. Soc. Faraday Trans. I* 86, 1363 (1990).
- Matijević, E., *J. Colloid Interface Sci.* 43, 214 (1973).
- Matsumoto, S., *J. Colloid Interface Sci.* 94, 362 (1983).
- Matsumoto, S. and Kang, W.W., *J. Dispersion Sci. Technol.* 10, 455 (1989).
- Metcalfe, I.M. and Healy, T.W., *Faraday Discuss. Chem. Soc.* 90, 335 (1990).
- Miller, C.A. and Neogi, P., "Interfacial Phenomena, Equilibrium and Dynamic Effects", Marcel Dekker, New York (1985).
- Milner, S.T., Witten, T.A., and Cates, M.E., *Macromolecules* 22, 2610 (1988).
- Morrison, I.D. and Ross, S., *J. Colloid Interface Sci.* 95, 97 (1983).
- Napper, D.H., "Polymeric Stabilization of Colloidal Dispersions", Academic, New York (1983).
- Nishimura, S., Chen, Z., Saswaki, H., and Usui, S., *J. Colloid Interface Sci.* 139, 238 (1990).
- Ohshima, H., *J. Colloid Interface Sci.* 162, 487 (1994).
- Ohshima, H., Chan, D.Y.C., Healy, T.W., and White, L.R., *J. Colloid Interface Sci.* 92, 232 (1983).
- Ohshima, H., Healy, T.W., and White, L.R., *J. Colloid Interface Sci.* 89, 484 (1982).
- Overbeek, T.Th.G., *J. Chem. Phys.* 64, 1178 (1960); *Pure Appl. Chem.* 52, 1151 (1980).
- Pashley, R.M. and Quirk, J.P., *Colloid Surfaces* 9, 1 (1984).
- Patel, S. and Tirrell, M., *Annu. Rev. Phys. Chem.* 40, 597 (1989).
- Platikanov, D., *J. Phys. Chem.* 68, 3619 (1964).
- Prins, A. and van den Tempel, M., *J. Phys. Chem.* 73, 2828 (1969).
- Rand, R.P. and Parsegian, V.A., *Biochim. Biophys. Acta* 988, 351 (1989).
- Russel, W.B., Saville, D.A., and Schowalter, W.R., "Colloid Dispersions", Cambridge University Press, Cambridge (1989).
- Sasaki, H., Matijević, E., and Barouch, E., *J. Colloid Interface Sci.* 76, 319 (1980).
- Scheludko, A., "Colloid Chemistry", Elsevier, Amsterdam (1966).
- Scheutjens, J.M.H.M. and Fleer, G.J., *J. Phys. Chem.* 83, 1919 (1979); *Macromolecules* 18, 1882 (1985).
- Spielman, L.A., *Annu. Rev. of Fluid Mech.* 9, 297 (1977).

- Tagawa, M., *Separation and Purification Methods* 15, 77 (1986).
- Takahashi, A. and Kawaguchi, M., *Adv. Poly. Sci.* 46, 1 (1982).
- Tamai, H., Hakozaki, T., and Suzawa, M., *Colloid Polym. Sci.* 258, 870 (1980).
- Tanner, R.I., "Engineering Rheology", Oxford University Press, Oxford (1985).
- Taunton, H.J., Toprakcioglu, C., Fetters, L.J., and Klein, J., *Macromolecules* 23, 571 (1990).
- Ternes, R.L. and Berg, J.C., *J. Colloid Interface Sci.* 98, 471 (1984).
- Tien, C. and Payatakes, A.C., *AIChE J.* 25, 735 (1979).
- Uemura, J., Matsumoto, M., Kawai, T., and Takenaka, T., *Can. J. Chem.* 63, 1713 (1985).
- Usui, S., Sasaki, H., and Hasegawa, F., *Colloids Surf.* 18, 53 (1986).
- Van Alsten, J. and Granick, S., *Macromolecules* 23, 4856 (1990).
- Vold, R.D. and Vold, M.J., "Colloid and Interface Chemistry", Addison-Wesley, Reading, Massachusetts (1983), p. 353.
- Wiese, G.R. and Healy, T.W., *J. Chem. Soc. Faraday Trans. 1* 66, 490 (1970).
- Yamanaka, T., Tano, T., Kamegaya, O., Exerowa, D., and Cohen, R., *Langmuir* 10, 1871 (1994).